

453. *Transition-metal Halide-Methyl Cyanide Complexes.*
*Part II.*¹ *Iron.*

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Iron reacts with chlorine and bromine in methyl cyanide to give crystalline complexes in which two-thirds of the iron is present as tetrahedral iron(III) and one-third as octahedral iron(II), as for example in $[\text{Fe}(\text{MeCN})_6]^{2+}[\text{FeBr}_4]^-$. Iodine oxidises iron wire to iron(II), producing $\text{FeI}_2 \cdot 3\text{MeCN}$, which is formulated as $[\text{Fe}(\text{MeCN})_6]^{2+}[\text{FeI}_4]^{2-}$. Iron(II) chloride and bromide form octahedral addition complexes with 2 and 4 molecules of methyl cyanide, these complexes are also formed by reduction, with iron powder, of the products from the halogen reactions. Inert atmospheres are necessary for all work connected with iron(II) in methyl cyanide. Iron wire also reacts with chlorine and bromine in ethyl acetate and nitromethane, but gives solid complexes only in the reactions with bromine. These products also contain two-thirds of the iron as tetrahedral iron(III), and the cations $[\text{Fe}(\text{EtAc})_6]^{2+}$ and $[\text{Fe}(\text{MeNO}_2)_6]^{2+}$, involving coordinated ethyl acetate and nitromethane. The structures of these complexes in the solid have been inferred from their reflectance spectra and magnetic properties. Spectra of solutions in methyl cyanide of tetrahedral iron(III) show no change on addition of halide ions, indicating negligible solvolysis. Jahn-Teller splitting of the spin-allowed band in octahedral iron(II) is discussed and an estimate of Δ for ethyl acetate and nitromethane has been obtained. An attempt is made to interpret the reflectance spectra of $[\text{FeX}_4]^-$.

THE chemistry of iron, in contrast to that of the metals discussed in Part I is complicated by the occurrence of two stable oxidation states, iron(II), d^6 , and iron(III), d^5 . In methyl cyanide solution, iron(II) complexes are very susceptible to oxidation and require the use of dry, inert atmospheres during their preparations. As in Part I, two main preparative routes have been used to study the ligand properties of methyl cyanide, namely anhydrous halides dissolved in methyl cyanide, and reactions between iron and halogens in methyl cyanide solution. The complexes obtained are listed in Table I, together with their colours and suggested stereochemistries. Halogens and iron wire also react in

¹ Part I, preceding Paper.

ethyl acetate and nitromethane, and the solids isolated from these reactions are also included.

Infrared Spectra.—Infrared (i.r.) spectra of the methyl cyanide complexes between 2200 and 2400 cm^{-1} indicate shifts in frequencies consistent with solvent co-ordination in all cases¹ (Table I). A number of complexes of some Group-(III) and -(IV) metal halides with ethyl acetate and other esters have been reported² and it has been shown from their i.r. spectra that co-ordination to the metal is through the carbonyl oxygen. Such co-ordination would (1) lengthen the C=O bond, decreasing the C=O stretching frequency, and (2) shorten the C-O bond, increasing the C-O stretching frequency. In co-ordination complexes of aldehydes and ketones,³ where bonding is definitely through the carbonyl oxygen, the C=O stretching frequency decreases by 50–150 cm^{-1} . Table I contains the i.r. frequencies of ethyl acetate and its compounds, supporting the above deductions. The shifts in our complexes of [Fe(II)] are 50% less than those observed by Lappert² in $\text{FeCl}_3 \cdot 2\text{EtAc}$, although in the latter case bonding occurs to a smaller, more highly charged ion and therefore should be stronger. Infrared spectra of nitromethane and the nitromethane complex are almost identical and the co-ordination must therefore be extremely weak and no clear evidence can be obtained from these results.

TABLE I.

Complex	Colour	Infrared spectra (cm^{-1})		μ (B.M.)		Structure
				obs.	r.m.s.	
$\text{FeCl}_3 \cdot 2\text{MeCN}$	red	2280	2305	5.95	—	oct.
$\text{FeCl}_2 \cdot 2\text{MeCN}$	off-white	2275	2285	—	—	oct.
$\text{FeBr}_3 \cdot 4\text{MeCN}$	brown	—	—	—	—	oct.
$[\text{Fe}(\text{MeCN})_6]^{2+}[\text{FeCl}_4]^-$..	yellow	2270	2290	5.92	5.86	oct-tet.
$[\text{Fe}(\text{MeCN})_6]^{2+}[\text{FeBr}_4]^-$..	deep red	2285	2305	5.89	5.86	oct-tet.
$[\text{Fe}(\text{EtAc})_6]^{2+}[\text{FeBr}_4]^-$..	brown	—	—	5.93	—	oct-tet.
$[\text{Fe}(\text{MeNO})_2]^{2+}[\text{FeBr}_4]^-$..	deep red	—	—	3.84	—	oct-tet.
$[\text{Fe}(\text{MeCN})_6]^{2+}[\text{FeI}_4]^{2-}$	dark green	2270	2290	5.48	5.49	oct-tet.
$(\text{Et}_2\text{N}^+)[\text{FeCl}_4]^-$	yellow	—	—	5.99	—	tet.
$(\text{Et}_4\text{N}^+)[\text{FeBr}_4]^-$	brown-red	—	—	5.99	—	tet.

Infrared spectra (cm^{-1}).		
	C-O	C=O
Ethyl acetate	1245	1745
$[\text{Fe}(\text{EtOAc})_6]^{2+}[\text{FeBr}_4]^-$..	1260–1280 (split)	1710
$\text{FeCl}_3 \cdot 2\text{EtOAc}$	1300	1656
Nitromethane	655s	923m 1100s
$[\text{Fe}(\text{MeNO})_6]^{2+}[\text{FeBr}_4]^-$..	655s	920m 1100s

Reflectance Spectra and Spectra of Solutions.—*Octahedral iron(II).* The ground state of iron(II), 5D , splits in a weak crystal field of octahedral symmetry into a lower $^5T_{2g}$ and an upper 5E_g level so that the spectra of octahedral iron(II) complexes consist of a fairly intense band at about 10,000 cm^{-1} . Some weak, spin-forbidden transitions have been observed⁴ between 20,000 and 26,000 cm^{-1} , but these have not so far been definitely assigned because the higher energy states 3P , 3H , and 3F lie very close together.

In several complexes the $^5E_g \leftarrow ^5T_{2g}$ transition is split, probably due either to Jahn-Teller distortions of the 5E_g level or to permanent distortion of the ion from O_h symmetry, as for example in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in ferrous ammonium sulphate.⁵ Liehr and Ballhausen⁶ have shown theoretically that Jahn-Teller splittings should be of the order of 1800–2000 cm^{-1} .

Tables 2 and 3 contain all the relevant spectral data for the complexes to be discussed.

² Lappert, *J.*, 1961, 817; 1962, 542.

³ Cassimatis and Susz, *Helv. Chim. Acta*, 1960, **43**, 852.

⁴ Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1502.

⁵ Cotton and Meyers, *J. Amer. Chem. Soc.*, 1960, **82**, 5023.

⁶ Liehr and Ballhausen, *Ann. Phys.*, 1958, **3**, 304.

No spin-forbidden transitions are observed in the spectrum $[\text{Fe}(\text{MeCN})_6](\text{BF}_4)_2$ ⁷ in methyl cyanide solution, and Fig. 1 shows the ${}^5E_g \leftarrow {}^5T_{2g}$ transition with broadening on the low-energy side. The reflectance spectrum, and the single crystal and solution spectra of $[\text{Fe}(\text{MeCN})_6][\text{FeCl}_4]_2$ are recorded in Table 2, and the reflectance spectrum shown in Fig. 1. All show a strong band, assigned to the ${}^5E_g \leftarrow {}^5T_{2g}$ transition in octahedral iron(II) between

TABLE 2.
Wave-numbers in cm^{-1} (extinction coefficients in parentheses).

<i>d-d</i> bands		Iron(III)							Iron(II)
		${}^4T_2 (F)$	${}^4T_1 (F)$	${}^4A_2 (F)$	${}^4E (D)$	${}^4T_2 (D)$	${}^4A_1, {}^4E (G)$	${}^4T_2, {}^4T_1 (G)$	
(a)	$[\text{FeCl}_4]^-$	22,200vs (32)		18,800s (1.4)	16,600sh (0.41)	16,100m (0.46)	14,500m (0.62)	13,700sh (0.46)	
	Reflectance	22,200vs	19,800sh	18,800s	16,500sh	16,100m	14,600m	13,800sh	
	$\left. \begin{array}{l} 0.425\text{M-Fe(II)} \\ 0.0850\text{M-Fe(III)} \end{array} \right\}$	22,200vs (32)		18,800s (1.7)	16,400sh (0.65)	16,000m (0.66)	14,500m (1.0)		10,900s (6.6)
(b)	Reflectance	22,200vs	19,800sh	18,800s	16,600sh	16,200m	14,400sh	11,500s	
	Single crystal			18,800s	16,400m		14,500m	10,500s	
(c)	$[\text{FeBr}_4]^-$		${}^4A_2 (F)$	${}^4T_1 (P)$	4E	4T_2	${}^4E_1, {}^4A_1 (G)$	${}^4T_1 (G)$	
	0.00173M	16,500s (58.0)	16,000sh (37.6)	14,500sh (28.2)	14,100s (32.7)	13,200sh (28.2)	12,700s (32.7)	11,700m (13.6)	
	Reflectance	16,400s	16,100sh	14,100m		13,000m		11,800sh	
(d)	$\left. \begin{array}{l} 0.0033\text{M-Fe(II)} \\ 0.0066\text{M-Fe(III)} \end{array} \right\}$	16,400s (40.2)	15,900sh (27.2)	14,300sh (19.4)	13,900s (23.5)	13,100sh (20.3)	12,700s (26.4)	11,600s (13.8)	9600sh (6.2)
	Reflectance	16,400s	16,100sh	14,100m		13,000s		11,800sh	10,000sh
	Single crystal	16,400s	15,900sh	14,300sh	13,900sh	13,000s		11,700sh	10,000sh
(e)	$\left. \begin{array}{l} 0.004\text{M-Fe(II)} \\ 0.008\text{M-Fe(II)} \end{array} \right\}$	16,400s (38.0)	15,900sh (25.0)	14,300sh (15.0)	14,000m (20.0)	13,100sh (18.0)	12,700s (25.0)	11,700b (17.0)	—
	Reflectance	16,400s	15,900sh	14,000sh		13,100b		11,800sh	10,000— 740vb
	$\left. \begin{array}{l} 0.0038\text{M-Fe(II)} \\ 0.0076\text{M-Fe(III)} \end{array} \right\}$	16,400s (45)	15,900sh (30.0)	14,300sh (25.0)	13,900s (29.0)	13,100sh (23.0)	12,700s (30.0)	11,700b (15.0)	10,000— 7000b
(f)	Reflectance	16,400s	15,900sh	14,000sh		13,000b		11,700sh	10,000— 7700b
	Ultraviolet bands.								
(a)	In very dilute methyl cyanide solution	47,400s	41,600s (600—10,000)	37,400sh	32,000s	27,700s			
(b)		48,000s	41,700s (600—10,000)	37,200sh	32,000s	27,600s			
(c)		45,400s	36,000s (10,000)	31,600sh	25,600m	23,500sh	21,300m		
(d)		45,400s	36,000s (10,000)	31,000sh	25,400m	23,600sh	21,200m		
(g)		48,000s	41,700s (6000—10,000)	37,300sh	32,000s	27,600s			

(a) = $\text{Et}_4\text{N}[\text{FeCl}_4]$; (b) = $\text{Fe}(\text{MeCN})_6[\text{FeCl}_4]_2$; (c) = $\text{Et}_4\text{N}[\text{FeBr}_4]$; (d) = $\text{Fe}(\text{MeCN})_6[\text{FeBr}_4]_2$; (e) = $\text{Fe}(\text{EtAc})_6[\text{FeBr}_4]_2$; (f) = $\text{Fe}(\text{MeNO}_2)_6[\text{FeBr}_4]_2$; (g) = $\text{FeCl}_3 \cdot 2\text{MeCN}$.

s = strong; m = medium; b = broad; sh = shoulder; v = very.

10,000 and 11,000 cm^{-1} , this being strong evidence for the $[\text{Fe}(\text{MeCN})_6]^{2+}$ ion, especially as the spectrum is identical with that of $(\text{Et}_4\text{N})[\text{FeCl}_4]$ ⁸ (Fig. 1) except for this band. The extinction coefficient (6.6) agrees well with the value of the tetrafluoroborate (6.0). The intensities of the main absorption bands in the spectra of the complexes $[\text{FeL}_6][\text{FeBr}_4]_2$ (where L = MeCN, EtAc, and MeNO₂), are 50—60 times greater than the intensities of those assigned to $[\text{FeCl}_4]^-$, this, coupled with the fact that absorptions in $[\text{FeBr}_4]^-$ occur at lower frequencies, means that bands due to $[\text{FeL}_6]^{2+}$ will only be seen as shoulders on the side of the much stronger absorptions. Since the ${}^5E_g \leftarrow {}^5T_{2g}$ transition corresponds to Δ , it is of interest to measure the band so that methyl cyanide, ethyl acetate, and nitromethane can be fitted into the spectrochemical series; but from the reflectance spectra in

⁷ Hathaway, Holah, and Underhill, *J.*, 1962, 2444.

⁸ Gill, *J.*, 1961, 3512.

Fig. 2 (curves A, B, and C) an accurate estimation is impossible. Experiments were then carried out with $(\text{Et}_4\text{N})[\text{FeBr}_4]^{-8}$ instead of magnesium oxide in the reference beam of the spectrophotometer in the hope that the spectrum due to $[\text{FeBr}_4]^{-}$ would be cancelled out. The technique was shown to be reliable by using $(\text{Et}_4\text{N})[\text{FeCl}_4]$ and $[\text{Fe}(\text{MeCN})_6][\text{FeCl}_4]_2$, where the ${}^5E_g \leftarrow {}^5T_{2g}$ transition is clearly visible in the spectrum of the latter. The results for the tetrabromo-complexes are shown in Fig. 2, and it therefore seems, as expected, that

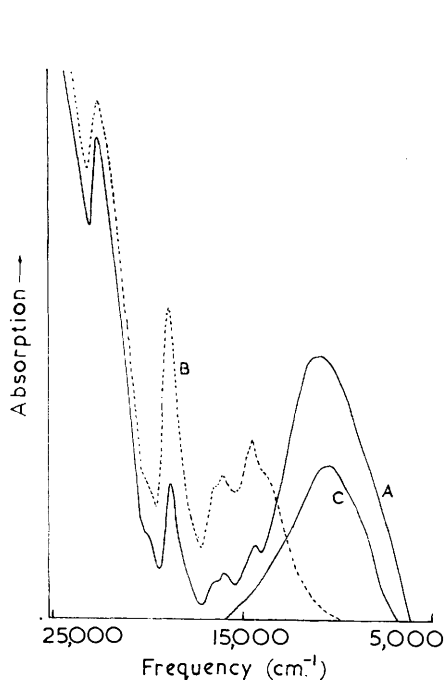


FIG. 1. The reflectance spectra of
A, $[\text{Fe}(\text{MeCN})_6][\text{FeCl}_4]_2$ and
B, $[\text{Et}_4\text{N}][\text{FeCl}_4]$,
and the spectrum (C) of a solution of
 $[\text{Fe}(\text{MeCN})_6](\text{BF}_4)_2$ in methyl cyanide.

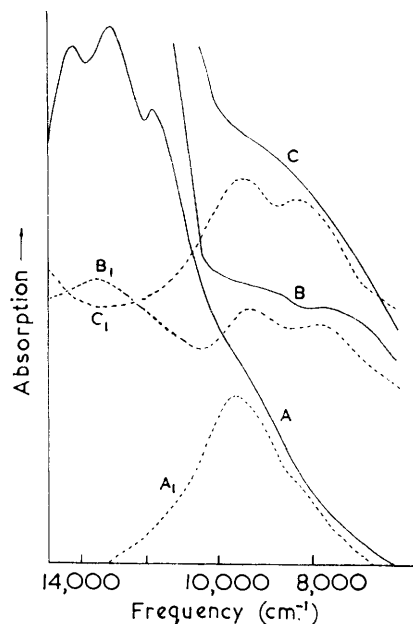
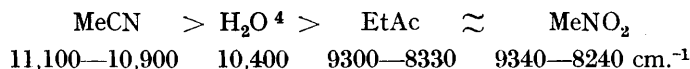


FIG. 2. The reflectance spectra of
some iron complexes,
A, $[\text{Fe}(\text{MeCN})_6][\text{FeBr}_4]_2$,
B, $[\text{Fe}(\text{EtOAc})_6][\text{FeBr}_4]_2$, and
C, $[\text{Fe}(\text{MeNO}_2)_6][\text{FeBr}_4]_2$.

The reflectance spectra of these complexes are shown in curves A₁, B₁, and C₁, when $[\text{Et}_4\text{N}][\text{FeBr}_4]$ was used as reference (see text).

ethyl acetate and nitromethane complexes have very similar Δ values, considerably lower than that of methyl cyanide complex. There is a slight discrepancy between the balanced spectrum and that of $[\text{Fe}(\text{MeCN})_6](\text{BF}_4)_2$,



the reason for which could be connected with the experimental conditions and nature of the surfaces.

In the unstable complex $\text{FeI}_2 \cdot 3\text{MeCN}$, formulated as $[\text{Fe}(\text{MeCN})_6][\text{FeI}_4]$ charge-transfer sets in at low energies so that only shoulders at 10,900 and 9500 cm.^{-1} due to the ${}^5E_g \leftarrow {}^5T_{2g}$ transition are observed. The reflectance spectrum into the infrared showed a steadily increasing absorption to about 5000 cm.^{-1} and the ${}^5E_g \leftarrow {}^5T_{2g}$ transition, which occurs⁹ at about 4000 cm.^{-1} in tetrahedral iron(II), was not observed.

⁹ Furlani, Cervone, and Valenti, *J. Inorg. Nuclear Chem.*, 1963, **25**, 159.

The reflectance spectrum of $\text{FeCl}_2 \cdot 2\text{MeCN}$ shows more detail in the visible region than do the octahedral complexes discussed above and has bands at 19,100, 20,800, 22,100, and 23,300 cm^{-1} . Jørgensen⁴ found similar bands in ferrous sulphate in sulphuric acid at 19,800, 21,100, 22,200, and 25,900 cm^{-1} , although these have not been assigned. The methyl cyanide complex also showed two very strong bands at 6330 and 9370 cm^{-1} , presumably due to splitting of the 5E_g level, although this is somewhat larger than the theoretical splitting calculated by Liehr and Ballhausen.⁶ Besides the Jahn–Teller effect, the complex in this case may also be distorted by non-equivalent ligands (cf., $\text{NiCl}_2 \cdot 2\text{MeCN}$ in ref. 1). $\text{FeBr}_2 \cdot 4\text{MeCN}$ was so unstable that no meaningful results were obtained.

TABLE 3.

${}^5E_g \leftarrow {}^5T_{2g}$ transitions in iron(II) complexes.			
Complex	Method *	Bands (cm^{-1})	Separation (cm^{-1})
$\text{Fe}(\text{MeCN})_6(\text{BF}_4)_2$	R	11,700—10,000vb	—
	S	10,900(max)—9400b	1500
$\text{Fe}(\text{MeCN})_6[\text{FeCl}_4]_2$	R	11,100vb	—
	B	10,900(max.)—9500b	1400
	S	10,900(max.)—9200b	1700
$\text{Fe}(\text{MeCN})_6[\text{FeBr}_4]_2$	R	10,000—9500b	—
	B	9710(max.)—8330sh	1380
	S	9600sh	—
$\text{Fe}(\text{MeNO}_2)_6[\text{FeBr}_4]_2$	R	10,000—7700vb	—
	B	9340(max.)—8240(max.)	1000
	S	—	—
$\text{Fe}(\text{EtAc})_6[\text{FeBr}_4]_2$	R	10,000—7400vb	—
	B	9300(max.)—8330sh	970
	S	—	—
$\text{Fe}(\text{MeCN})_6[\text{FeI}_4]$	R	10,900sh—9500sh	1400
$\text{Fe}(\text{EtAc})_6[\text{FeI}_4]$	R	9650sh—8400sh	1250
$\text{FeCl}_2 \cdot 2\text{MeCN}$	R	9370s—6330s	3040
$\dagger \text{Fe}(\text{H}_2\text{O})_6^{2+}$	R	10,800(max.)—8400sh	2400

* R, reflectance; B, reflectance, balanced with appropriate tetraethylammonium complex; S, solution, in appropriate solvent. vb, very broad; b, broad; sh, shoulder; s, strong.

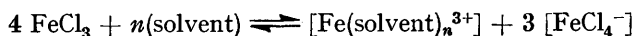
All these results on the spin-allowed transition in octahedral iron(II) complexes are collected in Table 3. Most of the splittings are between 1300 and 1700 cm^{-1} , slightly less than the calculated Jahn–Teller distortions.⁶ However, in view of the known distortion of $[\text{Fe}(\text{H}_2\text{O})_6^{2+}]$ in ferrous ammonium sulphate from regular octahedral symmetry it is possible that the $[\text{FeL}_6^{2+}]$ ions ($L = \text{MeCN}$, EtAc , and MeNO_2) are also slightly distorted as a result of packing in the crystal lattice, although there is no direct evidence for this.

Octahedral iron(III). Iron(III), being isoelectronic with manganese(II), d^5 , shows only very weak, spin-forbidden bands in the spectra of its complexes, and in complexes involving iron(III) halide many of these are obscured by charge-transfer bands which, in the chloro-complexes begin at 22,000—23,000 cm^{-1} and in the bromo-complexes at 17,000—18,000 cm^{-1} . It is possibly for this reason that charge-transfer bands in the ultraviolet spectrum have attracted so much interest,¹⁰ and though these bands have been used to identify $[\text{FeCl}_4^-]$ in solution, the exact nature of the electronic transitions is not understood.

The reflectance spectrum of $\text{FeCl}_3 \cdot 2\text{MeCN}$ shows only two bands, at 10,500, ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(S)$, and a shoulder at 14,300 cm^{-1} , ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(S)$, on the side of the charge-transfer absorptions. In methyl cyanide solution, as well as the weak band at 10,500 cm^{-1} , two shoulders appear at 14,500 and 13,700 cm^{-1} which become, on addition of chloride ions, the bands due to $[\text{FeCl}_4^-]$ (Table 2). Also the ultraviolet spectrum in very dilute methyl cyanide is identical with the spectrum of $(\text{Et}_4\text{N})[\text{FeCl}_4^-]$, having extinction coefficients between 6000 and 10,000. It appears therefore that solvolysis is occurring

¹⁰ Gamlen and Jordan, *J.*, 1953, 1435.

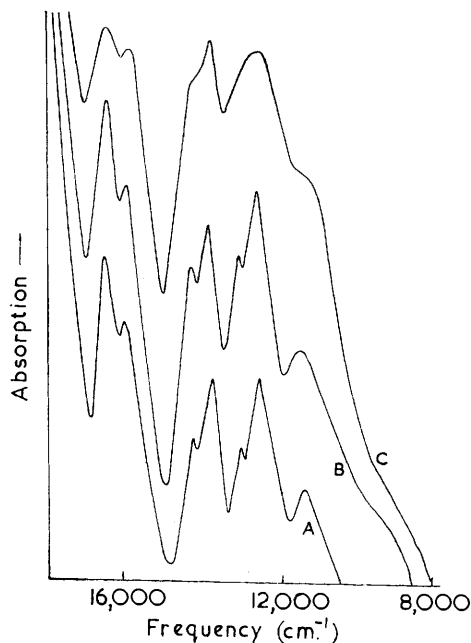
to produce the $[\text{FeCl}_4^-]$ ion, similar effects have been observed by Meek and Drago¹¹ when ferric chloride is dissolved in triethyl phosphate. A series of equilibria, which can be summarised as



was suggested to account for the formation of $[\text{FeCl}_4^-]$, and a similar situation is thought to exist in methyl cyanide solution.

Tetrahedral iron(III). Although a number of complexes containing $[\text{FeCl}_4^-]$ and $[\text{FeBr}_4^-]$ are known, and the former ion has in fact been shown by X-ray crystallographic analysis to be very close to a regular tetrahedron,¹² their spectra, which have been reported,⁸ have not been fully interpreted.¹³ From Orgel's diagram of d^5 systems,¹⁴ there are ten expected transitions, of which seven are visible in the solution spectra of $(\text{Et}_4\text{N})[\text{FeBr}_4]$ ⁸ and $[\text{Fe}(\text{MeCN})_6][\text{FeBr}_4]_2$ shown in Fig. 3, the two spectra differing only

FIG. 3. The spectra in methyl cyanide solution of
A, $(\text{Et}_4\text{N})[\text{FeBr}_4]$ and
B, $[\text{Fe}(\text{MeCN})_6][\text{FeBr}_4]_2$.
The single-crystal spectra of
C, $[\text{Fe}(\text{MeCN})_6][\text{FeBr}_4]_2$.



in the shoulder about $10,000 \text{ cm}^{-1}$ due to $[\text{Fe}(\text{MeCN})_6^{2+}]$. Fig. 3 also contains the single-crystal spectrum of the latter although in this, and in the reflectance spectrum, the bands are not so clearly resolved as they are in solution. The spectra of solutions agree with the details published by Gill,⁸ and show no change on addition of Et_4NBr .

The ten transitions in octahedral manganese(II) complexes occur between $18,000$ and $40,000 \text{ cm}^{-1}$,^{1,13} and help in assigning these is obtained by considering the three sharp bands which are transitions to the three levels on Orgel's diagram independent of Δ .^{15,16} Seven of the ten transitions in iron(III) complexes are observed between $11,000$ and $17,000 \text{ cm}^{-1}$, which means a large decrease in term separations due to more covalency

¹¹ Meek and Drago, *J. Amer. Chem. Soc.*, 1961, **83**, 4322.

¹² Zaslow and Rundle, *J. Phys. Chem.*, 1957, **61**, 490.

¹³ Jørgensen, "Absorption Spectra and Chemical Bonding Complexes," Pergamon Press, London, 1962, p. 292.

¹⁴ Dunn, "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience, Publ. Inc., New York, 1960, p. 229.

¹⁵ Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

¹⁶ Furlani and Furlani, *J. Inorg. Nuclear Chem.*, 1960, **19**, 51.

associated in the bonding in the higher charged, tetrahedral ions. This, together with the decrease in Δ , means that several of the levels have energies almost independent of Δ , resulting in six very sharp bands (Fig. 3). The first three bands, at 11,600, 12,700, and 13,100 cm^{-1} are assigned to transitions to the 4G sub-levels, to ${}^4T_1(G)$, ${}^4T_2(G)$, and ${}^4E, {}^4A_1$, respectively. The next transitions, at 13,900 and 14,300 cm^{-1} could be due to the ${}^4T_2(D)$ and ${}^4E(D)$, respectively, while the remaining two at 15,900 and 16,400 cm^{-1} are to the 4P or 4F levels. The percentage decreases in term separations have been calculated by assuming this interpretation, and are compared with the figures for manganese(II) in Table 4. Interpretation of the spectrum of $[\text{FeCl}_4^-]$ is even more uncertain, as this is

TABLE 4.
Term separations in cm^{-1} . (Percentage decreases in complexes.)

State	Manganese(II)			Iron(III)			
	Mn ²⁺ free ion	Mn(H ₂ O) ₆ ²⁺	MnI ₄ ²⁻	Fe ³⁺ free ion	Fe(H ₂ O) ₆ ³⁺	FeBr ₄ ⁻	FeCl ₄ ⁻
	Ref. 17	Ref. 13	0	Ref. 17	Ref. 4	0	0
⁶ S	0	0	0	0	0	0	0
⁴ G	26,800	25,000(7.0)	22,200(17.0)	32,000	24,600(23.0)	13,000(59.0)	14,600(54.4)
⁴ D	32,300	29,700(8.0)	26,700(17.4)	38,500		14,300(62.7)	16,500(57.2)
⁴ F	43,600	35,400(19.0)	32,100(26.4)	52,100		16,400(68.6)	18,800(63.9)

rather less clearly resolved (Fig. 1). Jørgensen¹³ interpreted the strong sharp band at 18,800 cm^{-1} as the ${}^6S \rightarrow {}^4G$ separation, *i.e.*, the ${}^4E_1, {}^4A_1(G) \leftarrow {}^6A_1(S)$ transition, but if this is correct, it is difficult to account for the four transitions occurring at lower energies. It seems more likely that either the 14,500 or the 16,100 cm^{-1} band is the transition to the ${}^4E(D)$ or ${}^4A_2(F)$ states. By comparison with the spectrum of the $[\text{FeBr}_4^-]$ ion the assignments of the spectrum of the $[\text{FeCl}_4^-]$ ion shown in Table 2 are considered to be the most likely. The percentage reduction in the term separation, from the free ion to the complexed ion, are given in Table 4; the smaller decrease for the $[\text{FeCl}_4^-]$ ion compared to $[\text{FeBr}_4^-]$ is consistent with a higher degree of covalent bonding in the latter ion, as the bromide ion lies higher in the nephelauxetic series than the chloride ion.¹³

Ginsberg and Robin¹⁸ have very recently reported the spectrum of the $[\text{FeCl}_4^-]$ and $[\text{FeBr}_4^-]$ ions as thin films at 20°K and comment on the poor quality of the published spectra of solution of these ions. At low temperature slightly better resolution was obtained, producing at least one more band for each anion. Numerically the two sets of data agree closely, and for the spectrum of the $[\text{FeBr}_4^-]$ ion the agreement on the independent assignment of this spectrum gives some confidence in this assignment although both are speculative. For the $[\text{FeCl}_4^-]$ ion both sets of data are less clearly resolved, but agree on a reasonable assignment which is different to that put forward by Jørgensen¹⁷ for this anion.

The extinction coefficients for these iron complexes increase from 0.5–1.0 in the $[\text{FeCl}_4^-]$ ion to 6–7 for the spin-allowed band in $[\text{Fe}(\text{MeCN})_6^{3+}]$, and to 20–30 in $[\text{FeBr}_4^-]$. Therefore, isolation of complexes of the type $[\text{FeL}_6^{2+}][\text{FeCl}_4^-]_2$, where L = EtAc or MeNO₂, would yield more information regarding the ${}^5E_g \leftarrow {}^5T_{2g}$ transition in $[\text{FeL}_6^{2+}]$ to lend support to the information already obtained on the reflectance spectra of the bromo-complexes (Fig. 2). The reaction between iron wire and chlorine occurs in both solvents and although no solid was obtained, the spectra of the solutions showed evidence for $[\text{FeCl}_4^-]$ in the form of bands at 18,800, 16,600, 16,000, and 14,600 cm^{-1} , but no evidence of the ${}^5E_g \leftarrow {}^5T_{2g}$ band in $[\text{FeL}_6^{2+}]$ could be found.

Other properties. The magnetic moments are shown in Table 1. Octahedral and tetrahedral iron(III) complexes are expected to have moments very close to the spin-only

¹⁷ "Atomic Energy Levels," ed. Moore, U.S. Bureau Stand., Circ. No. 467, 1952, p. 65.

¹⁸ Ginsberg and Robin, *Inorg. Chem.*, 1963, 2, 817.

value (5.92 B.M.), due to the $6S$ ground state, and for some of the mixed oxidation-state complexes, root-mean-square values have been calculated from the constituents, *e.g.*, the observed moment of $[\text{Fe}(\text{MeCN})_6][\text{FeBr}_4]_2$ is 5.89 B.M., while the root-mean-square moment calculated from $[\text{Fe}(\text{MeCN})_6](\text{BF}_4)_2$, 5.59 B.M., and $(\text{Et}_4\text{N})[\text{FeBr}_4]$, 5.99 B.M., is 5.86 B.M., in excellent agreement. $\text{FeCl}_3 \cdot 2\text{MeCN}$ and $\text{FeBr}_2 \cdot 4\text{MeCN}$ were too unstable for accurate measurement, but $\text{FeI}_2 \cdot 3\text{MeCN}$ has a value in good agreement with the root-mean-square of $[\text{Fe}(\text{MeCN})_6](\text{BF}_4)_2$ and $(\text{Et}_4\text{N})_2[\text{FeI}_4]$. The complexes $[\text{FeL}_6](\text{BF}_4)_2$, where $\text{L} = \text{EtAc}$ and MeNO_2 , are not known, so that the root-mean-square moments cannot be compared with the observed moments in complexes containing these ions.

It has already been shown that the solution spectra in methyl cyanide of mixed oxidation-state complexes indicate negligible solvolysis, making conductivities in methyl cyanide meaningful. $[\text{Fe}(\text{MeCN})_6^{2+}][\text{FeCl}_4^-]_2$ and $[\text{Fe}(\text{MeCN})_6^{2+}][\text{FeBr}_4^-]_2$ both have conductivities of $250 \text{ ohm}^{-1} \text{ cm}^2$ in 0.1M -solution in methyl cyanide, compared with $150 \text{ ohm}^{-1} \text{ cm}^2$ for a 1 : 1 electrolyte, Et_4NBr , and $230 \text{ ohm}^{-1} \text{ cm}^2$ for a 2 : 1 electrolyte, such as $(\text{Et}_4\text{N})_2[\text{CoBr}_4]$, at the same concentration and temperature in methyl cyanide,¹ fully supporting the above formulation for the iron complexes.

General discussion. Although only two bands in the spectrum of $\text{FeCl}_3 \cdot 2\text{MeCN}$ have been observed, its structure in the solid is clearly octahedral, probably dimeric, with bridging halides. It has been shown that solvolysis occurs in methyl cyanide solution, and evidence points to the formation of $[\text{FeCl}_4^-]$; in fact, on addition of Et_4NCl , the complex $(\text{Et}_4\text{N})[\text{FeCl}_4]$ can be prepared. It has been reported¹⁹ that when ferric chloride is dissolved in acrylonitrile, one third of the iron is reduced to iron(II), accompanied by chlorination of the solvent. Golden yellow crystals were obtained and analysis indicated an empirical formula similar to our complex. We have repeated the preparation and measured the reflectance spectrum of the complex which is consistent with a formulation as $[\text{Fe}(\text{acrylonitrile})_6^{2+}][\text{FeCl}_4^-]_2$. The great stability of the $[\text{FeCl}_4^-]$ and $[\text{FeBr}_4^-]$ ions is probably connected with the d^5 configuration; the stability of the $[\text{FeBr}_4^-]$ is reflected by the fact that it will stabilise such ions as $[\text{Fe}(\text{EtAc})_6^{2+}]$ and $[\text{Fe}(\text{MeNO}_2)_6^{2+}]$, the i.r. spectra of which show the solvents to be only weakly co-ordinated. Nitromethane is often used as an "inert solvent" for conductivity measurements at very dilute concentrations, but in view of our findings that the solvent almost certainly co-ordinates, some caution should be used in interpreting results obtained in this solvent. Nitromethane is also a good solvent for many anhydrous transition-metal salts, another indication that solvolysis is occurring in solution. It is surprising that similar complexes do not occur with $[\text{FeCl}_4^-]$; why this should be is not known but it may be determined by the relative sizes of the ions and their crystal packing effects.

The complexes $\text{FeCl}_2 \cdot 2\text{MeCN}$ and $\text{FeBr}_2 \cdot 4\text{MeCN}$ are in keeping with those of manganese and nickel described in Part I, the first complex being octahedral with bridging halides, while the second is very unstable. Although no direct evidence has been obtained for the structure $[\text{Fe}(\text{MeCN})_6][\text{FeI}_4]$, it seems a reasonable structure, especially considering similar complexes with manganese, cobalt, and nickel.¹ In the reaction of iron wire with the halogens in an organic solvent, it is understandable why iodine only produces iron(II) complexes as iodine is a less-powerful oxidising agent than chlorine or bromine. But given that chlorine and bromine will oxidise iron(II) to iron(III) it is difficult to understand why complexes of mixed oxidation states occurs, especially as ferric chloride will form a stable bis(methyl cyanide) complex. The common features of these complexes of mixed oxidation state is the presence of the tetrahalogenoferrate(III) anion; this must be sufficiently stable both to prevent complete oxidation of all the iron to iron(III) and to form six co-ordinate iron(II) complexes involving the very weakly donor ligands ethyl acetate and nitromethane which have not been reported previously as ligands in six-coordinate complexes. Further evidence of the inherent stability of the tetrahalogenoferrate(III) anions is their resistance to solvolysis in methyl cyanide solution compared to the ready solvolysis of the bivalent tetrahedral anions described in Part I.

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EXPERIMENTAL

Methyl cyanide was purified and dried as described in Part I, ethyl acetate was distilled from phosphorus pentoxide, and nitromethane was fractionally distilled after storage over dried sodium sulphate.

General methods of preparation were outlined in Part I, but in some of the iron reactions, inert atmospheres were needed. Reactions, reductions, Soxhlet extractions, and filtrations were carried out in closed "Quickfit" apparatus under nitrogen.

Trichlorobis(methyl cyanide)iron(III).—Anhydrous ferric chloride was dissolved in methyl cyanide (10 ml.), and the hot saturated solution was filtered. Excess of methyl cyanide was removed under vacuum, giving a red, extremely hygroscopic solid. Iron was estimated as Fe_2O_3 , and the halide as AgCl (Found: Fe, 22.9; Cl, 43.5. $\text{FeCl}_3 \cdot 2\text{CH}_3\text{CN}$ requires Fe, 22.9; Cl, 43.6%).

Dichlorobis(methyl cyanide)iron(II).—Iron(II) chloride (5 g.) was extracted with methyl cyanide (50 ml.) in a Soxhlet under nitrogen. Alternatively, the product from the reaction between iron wire (3 g.) and chlorine in methyl cyanide was reduced by refluxing it with iron powder, giving off-white crystals. Iron was estimated by immediate titration with permanganate, and the halide as above (Found: Fe, 26.6; Cl, 33.9. $\text{FeCl}_2 \cdot 2\text{CH}_3\text{CN}$ requires Fe, 26.7; Cl, 34.0%).

Dibromotetrakis(methyl cyanide)iron(II).—This was prepared as above, iron(II) bromide being used for the Soxhlet extraction, or by the reaction between iron wire and bromine, followed by reduction. The complex formed pale brown unstable crystals which rapidly turn brown in air. Iron was estimated as Fe_2O_3 and the halide as above (Found: Fe, 14.6; Br, 43.25. $\text{FeBr}_2 \cdot 4\text{CH}_3\text{CN}$ requires Fe, 14.7; Br, 42.1%).

Hexakis(methyl cyanide)iron(II) Bistetrachloroferrate(III).—Iron wire (3 g.), chlorine, and methyl cyanide (30 ml.) were allowed to react under nitrogen. Yellow crystals of complex were purified by recrystallisation from methyl cyanide. The total iron, Fe(T) was estimated as Fe_2O_3 , iron(II) by immediate titration with permanganate, iron(III) volumetrically with potassium iodide-thiosulphate, and halide as above [Found: Fe(T), 24.1; Fe(II), 8.05; Fe(III), 16.0; Cl, 40.7; C, 20.3; H, 2.7. $\text{Fe(III)}_2\text{Fe(II)Cl}_8 \cdot 6\text{CH}_3\text{CN}$ requires Fe(T), 24.0; Fe(II), 8.0; Fe(III), 16.0; Cl, 40.7; C, 20.7; H, 2.6%].

Hexakis(methyl cyanide)iron(II) Bistetra bromoferrate(III).—The procedure was as above, iron wire, bromine (3 ml.), and methyl cyanide being used. (It was not necessary to carry out this reaction under nitrogen.) Iron(II) was estimated with permanganate immediately after precipitation of bromide with silver nitrate [Found: Fe(T), 15.9; Fe(II), 5.2; Fe(III), 10.4; Br, 60.5; C, 13.7; H, 1.8; N, 8.1. $\text{Fe(III)}_2\text{Fe(II)Br}_8 \cdot 6\text{CH}_3\text{CN}$ requires Fe(T), 15.9; Fe(II), 5.3; Fe(III), 10.6; Br, 60.7; C, 13.7; H, 1.7; N, 8.0%].

Hexakis(ethyl acetate)iron(II) Bistetra bromoferrate(III).—The procedure was as above, ethyl acetate being used instead of methyl cyanide [Found: Fe(T), 12.6; Fe(II), 4.1; Fe(III), 8.3; Br, 48.0. $\text{Fe(III)}_2\text{Fe(II)Br}_8 \cdot 6\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ requires Fe(T), 12.6; Fe(II), 4.2; Fe(III), 8.4; Br, 47.9%].

Hexakis(nitromethane)iron(II) Bistetra bromoferrate(III).—The procedure was as above, nitromethane being used instead of ethyl acetate [Found: Fe(T), 14.3; Fe(II), 4.7; Fe(III), 9.4; Br, 54.4. $\text{Fe(III)}_2\text{Fe(II)Br}_8 \cdot 6\text{CH}_3\text{NO}_2$ requires Fe(T), 14.3; Fe(II), 4.8; Fe(III), 9.5; Br, 54.5%].

Hexakis(methyl cyanide)iron(II) Tetraiodoferrate(II).—Iron wire (3 g.), iodine (2 g.), and methyl cyanide were refluxed for 2 hr. under nitrogen, and the dark green crystals of complex were recrystallised from methyl cyanide. Iron was estimated as Fe_2O_3 and the halide as above (Found: Fe, 12.8; I, 58.0; C, 16.4; H, 2.2. $\text{FeI}_2 \cdot 3\text{CH}_3\text{CN}$ requires Fe, 12.9; I, 58.4; C, 16.6; H, 2.1%).

Physical Properties.—Infrared and reflectance spectra, magnetic moments, and electrical conductivities were measured as in Part I. Spectra of solutions and single crystals were measured by using a Unicam S.P. 700 recording spectrophotometer.

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¹⁹ Kern, *J. Inorg. Nuclear Chem.*, 1963, 25, 5.